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(54) Phosphate composition and uses thereof.

(57) The brightness of hydrogen peroxide bleached cellulosic material e.g. mechanical wood pulp or fabrics may be increased if the cellulosic material is contacted with both phosphoric acid, or a salt thereof, and an amino phosphonic acid or a salt thereof.

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PHOSPHATE COMPOSITION AND USES THEREOF

This invention relates to phosphate compositions, in particular ones for use in stabilising hydrogen peroxide.

Hydrogen peroxide is used to bleach cellulosic materials e.g. wood pulp or fabrics, but the effectiveness of the bleaching liquor is reduced in the absence of stabilisers against decomposition of the peroxide by transition metal ion e.g. iron and manganese in the cellulosic material or water. The commercially accepted stabiliser is sodium silicate but this gives rise to other problems e.g. corrosion and scaling. Phosphonates especially diethylene triamine penta (methylene phosphonic acid) and its water soluble salts have been proposed as stabilisers, but with pulps having significant metal contents or made with hard water the degree of bleaching (as shown by the brightness of the cellulosic material) and/or the peroxide stability is reduced.

We have discovered how to increase the stability and/or the brightness with phosphonates.

The present invention provides a stabilised peroxide composition which comprises component (a) hydrogen peroxide, component (b) which is a water soluble amino organic phosphonic acid with at least 2 organo phosphonic acid groups, or a water soluble salt thereof, and component (c) which is orthophosphoric acid or a water soluble salt thereof.

There is also provided a method of bleaching a cellulosic material with hydrogen peroxide, wherein the cellulosic material is contacted with an aqueous alkaline solution comprising as component (a) the hydrogen peroxide, component (b) which is a water soluble amino phosphonic acid, or water soluble salt of an amino phosphonic acid, and component (c) which is orthophosphoric acid or a water soluble orthosphosphate salt. There is also provided a pulp bleaching medium which comprises an aqueous medium containing a cellulosic pulp and a composition which comprises component (a) hydrogen peroxide, component (b) which is a water soluble amino organic phosphonic acid with at least 2 organo phosphonic acid groups, or a water soluble salt thereof, and component (c) which is orthophosphoric acid or a water soluble salt thereof.

The use of a mixture of the phosphonic acid (or salt) with orthophosphoric acid (or salt) as a stabiliser for hydrogen peroxide in the bleaching of cellulosic material is also included.

The amino phosphonic acid contains primary secondary or tertiary amine groups, especially with amino groups only of the tertiary type, and at least 2 and usually 2-10 especially 3-6 organophosphonic acid groups; while the molecule may contain acidic groups other than phosphonic acid groups, such as carboxylic acid groups, these are preferably absent.

The aminoorganic phosphonic acid may be of formula 1

$$H_2O_3PCR^1R^2N(R^3)[R^4N(R^7)]_nCR^5R^6PO_3H_2 \quad (I)$$

wherein each of R^1, R^2, R^5, R^6, which is the same or different, represents a hydrogen atom or an optionally substituted aliphatic hydrocarbyl, alicyclic, aryl or aralkyl group, each preferably of 1-20, especially 1-8, carbon atoms for the aliphatic group or 5-10 carbon atoms in respect of alicyclic, aryl or aralkyl group, and each of R^3 and R^7, which is the same or different, is as defined for any one of R^1, R^2, R^5 and R^6 apart from hydrogen, or is a group of formula

$-C(R^8)(R^9)PO_3H_2$

wherein each of R^8 and R^9, which may be the same or different, is as defined for any of R^1, R^2, R^5 or R^6, and R^4 represents a divalent organic group eg of 1-10 carbon atoms, n is 0 or an integer of at least 1 e.g. 1-5 such as 1 or 2. The aliphatic hydrocarbyl group may be an alkyl or alkenyl group, such as methyl, ethyl, propyl or isopropyl group, butyl, amyl, hexyl, octyl, decyl or dodecyl group. Examples of the optional substituents are one or more alkoxy groups e.g. of 1-8 carbon atoms, hydroxy and halo groups. The alicyclic group may be a cyclopentyl or cyclohexyl group, while the aryl group may be a phenyl or naphthyl group which may optionally be substituted by at least one alkyl eg methyl, halo eg chloro or nitro substituent. The aralkyl group may be a benzyl or naphthylmethyl group, optionally substituted by at least one alkyl eg methyl, halo eg chloro or nitro substituent. Preferably R^1, R^5, and R^9 if present, represent hydrogen atoms, and R^2, R^6 and R^8 if present, represent hydrogen atoms or alkyl or aryl eg phenyl or tolyl group. Most preferably each of R^1, R^2, R^5, R^6 and if present, R^8 and R^9 represent hydrogen atoms, while R^3 and R^7 preferably represent an alkyl group of 1-4 carbon atoms or alkoxyalkyl group e.g. 4-14 carbon atoms or the group of formula

$-C(R^8)(R^9)PO_3H_2$

The divalent group or groups R^4 may be an alkylene group eg of 1-6 carbon atoms such as 1,2 ethylene, 1-3 - propylene, 1,4 - butylene or 1,6-hexylene or other alpha, omega alkylene group, or phenylene eg 1,2 or 1,4 phenylene or cyclohexylene eg 1,1 or 1,4-cyclohexylene. Preferably R^4 is an ethylene group.

Thus preferred compounds are amino tris (methylene phosphonic acid), ethylene diamine tetra

(methylene phosphonic acid) and other alkylene alpha, omega diamine tetra (methylene phosphonic acids), diethylene triamine penta(methylene phosphonic acid) (hereafter called DTPMPA) and triethylene tetramine hexa (methylene phosphonic acid), and other polyamine poly (alkylene phosphonates).

These crude amino organo phosphonic acids, made from the amine, aldehyde or ketone and phosphorous acid, preferably contain a majority of the desired phosphonic acid product eg 50-100% especially 50-80% and usually a minority of amino phosphonic acids with less than the optimum proportion of phosphonic acid groups per nitrogen atom; these other compounds can contain N-H groups or N-methyl groups in replacement of one or more but not all of the organo-phosphonic acid groups.

In this specification, unless otherwise stated, the percentage of amino organo phosphonic acids is expressed on the assumption that all acid species are amino organo phosphonic acids and that all the latter have organo phosphonate groups replacing every hydrogen atom bonded to a nitrogen atom in the amine of formula

$H[N(R^3)R^4)_nNHR^7$

wherein R^4 is as defined above and each of R^3 and R^7 is as defined for R^1. The analyses for the acid species can be performed by base titration.

The amino phosphonic acid may be present as the free acid but is preferably present as a water soluble partial or completely neutralised salt thereof e.g. an ammonium, organic ammonium, sodium or potassium salt, such as ones with 10-90% of the acidic hydrogen atoms repiaced by the salt cation. Aqueous solution of the salts preferably have a pH of 0.5-10.

The phosphate component may be orthophosphoric or a water soluble salt thereof e.g. an alkali metal salt especially a sodium or potassium salt. The salt may be a mono di or tri alkali metal salt, among which mono sodium di hydrogen phosphate and/or di potassium hydrogen phosphate are preferred. When phosphoric acid is used, extra alkali e.g. sodium hydroxide solution is added prior to the bleach operation.

The weight proportion of phosphoric acid (or pro rata amounts of orthophosphate salt) to the amino phosphonic acid, especially ones of formula 1, (or pro rata amounts of the salts) is usually at least 0.5:1 preferably at least 1.5:1 e.g. 0.5:1 to 20:1 such as 1.5-20:1, 1.5-16:1 or in particular 2-20:1 e.g. 2-10:1 and especially 2-5:1; proportions of 6.75-10:1 may also give benefits. These proportions are particularly important for di ethylene triamine penta methylene phosphonic acid (hereinafter called DTPMPA) as the amino phosphonic acid, but also apply generally to other amino phosphonic acids either as such, or in pro rata amounts based on equal moles of the other amino phosphonic acid to DTPMPA. Thus the pro rata amounts based the ratio of the number of moles of phosphoric acid (or pro rata amounts of orthophosphate salt) to the number of moles of amino phosphonic acid, especially ones of formula 1, (or pro rata amounts of the salts) is usually at least 2.92:1 preferably at least 8.77:1 e.g. 2.92:1 to 117:1 such as 8.77-117:1, 8.77-93.5:1 or in particular 11.7-117:1 e.g. 11.7 - 58.5:1 and especially 11.7-29.2:1.

The proportion of phosphoric acid (or pro rata amounts of phosphate salt) to the amino phosphonic acid, (or pro rata amounts of the salts) is usually from 1.75 to 23.4:1 e.g. 2.34 to 23.4:1 in terms of the ratio of phosphorus atoms present in total in each category of compound.

The stabiliser compositions, the stabilised composition of (a), (b) and (c) and the peroxide bleaching liquor or medium may also contain other additives used in peroxide bleaching liquors, such as inorganic e.g. sodium pyro and poly phosphates, but are usually substantially free of monomeric polyhydroxy carboxylic acids or amino poly carboxylic acids such as hydroxy aliphatic carboxylic acids such as gluconic or citric acid, amino polycarboxylic acids e.g with 2-6 carboxyl groups per molecule such as nitrilo triacetic acid, ethylene diamine tetraacetic acid, diethylene triamine penta acetic acid; the cellulose material itself may contain polymeric poly carboxylic acids and these may still be present. Preferably the stabiliser and stabilised compositions and the peroxide bleaching liquor and medium are also substantially free from water soluble silicates such as sodium silicates and from pyro and poly phosphates. Preferably other compounds apart from the phosphonic acid (or salt) and phosphoric acid (or salt), having a stabilising effect on hydrogen peroxide in pulp bleaching are substantially absent also. Thus the stabiliser composition for stabilizing the hydrogen peroxide preferably consists essentially of the phosphonic acid (or salt), phosphoric acid (or salt) and water.

The stabiliser composition for mixing with the hydrogen peroxide to produce the stabilized peroxide composition or for adding in the production of the bleaching medium is usually in aqueous solution e.g. at pH 0.5-10 preferably 3-10, and often contains 2-20% e.g. 5-15% of the amino phosphonic acid, and 10-70% e.g. 10-45% and especially 15-40% of the phosphoric acid (expressed as anhydrous acid), with the remainder being usually substantially water.

The cellulosic material to be bleached may be in the form of individual fibres e.g. as in wood pulp or cotton fibres, or as yarn or woven or non woven fibres and includes wood, cotton, linen and jute and loose fibrous products obtained therefrom, but especially wood pulp, whose treatment is hereinafter exemplified.

The pulp to be bleached is usually made by mechanical treatment, especially stoneground (SGW) thermomechanical (TMP) or chemithermomechanical pulping (CTMP) followed by scr ening of oversize material, optionally washing with water and then usually dilution with water and/or bleach liquor to the concentration ready for the bleaching step. The pulp may also have been derived from secondary pulp from deinked used paper products. The invention is of particular value when the water used in the production of the pulp is hard water, so the pulp has a significant calcium and/or magnesium content e.g. a total of Ca and Mg of at least 800 such as 1000-2500 especially 1000-2000 ppm (based on the oven dried weight of the pulp before dilution and bleaching). The invention is also of particular value with pulps having substantial amounts of calcium or at least 80 ppm total transition metals e.g. 80-350 ppm, usually with at least 50 ppm of Fe and/or Mn (based on the oven dried weight of pulp). The alkaline earth and transition metal ions are derived from the cellulosic material or the water or both. The water of dilution may be fresh soft or hard water or may be recycled plant water e.g. recycled bleach liquor or paper machine white water.

The amino phosphonic acid or salt and the phosphoric acid (or salt) may be added to the cellulosic material separately or together in the form of the stabiliser composition with adjustment of the pH to 8-12 e.g. 10-12 by addition of alkali; they may be added directly to the cellulosic material e.g. wet pulp before addition of hydrogen peroxide to give a bleach medium containing cellulosic material and aqueous bleach liquor in contact therewith. The amount of each additive in the bleach medium varies according to the nature of the pulp to be treated, the degree of bleaching desired, the amount of hydrogen peroxide, the hardness of the water and the transition metal content of the pulp, increases on the last 4 parameters usually requiring more additive. However, usually the amount of the phosphonic acid (or salt) (expressed as phosphonic acid) is 0.01-1% e.g. 0.02-0.5% and especially 0.04-0.3% and the amount of the phosphoric acid (or salt) (expressed as phosphoric acid) is 0.05-2% e.g. 0.05-1% especially 0.1-0.8% e.g. 0.22-0.8%, while the total of phosphonic acid and phosphoric acid in the bleaching medium is usually at least 0.1% especially at least 0.2% such as 0.2-3% or 0.2-1%, especially at least 0.22% e.g. 0.25-0.7%, in all cases based on the dry weight of cellulosic material e.g. pulp in the bleach medium. In relation to the total volume of the bleach medium, the amount of phosphonic acid (or salt) is usually 0.01-1.5g/l e.g. 0.03-0.8 or 0.06-0.5g/l, the amount of phosphoric acid (or salt) is usually 0.08-3g/l e.g. 0.08-1.5g/l or 0.15-1g/l and the total of phosphonic acid (or salt) and phosphoric acid (or salt) is usually at least 0.15g/l e.g. at least 0.3g/l such as 0.3-4.5g/l or 0.3-1.5g/l especially 0.35-1.1g/l.

The pulp is bleached with hydrogen peroxide which is usually present in amount of 0.5-10% especially 1-5% (based on the dry weight of the pulp); compounds decomposable in the bleach liquor to hydrogen peroxide may also be used in equivalent amounts. In relation to the amount of hydrogen peroxide in the bleach liquor, the amount of the phosphonic acid (or salt) is usually 1-15% e.g. 1-10% especially 2-10% e.g. 2-6%, the amount of phosphoric acid (or salt) is usually 5-35% e.g. 8-25% such as 8-15% and the total of phosphonic acid (or salt) and phosphoric acid (or salt) is usually 10-40% such as 10-30% especially 10-20%. The pulp in the bleaching operation usually has a cellulosic material solids content (herein-after called the pulp consistency) of 10-50% preferably 10-35%. The bleach medium containing the wet pulp may contain at least 5 ppm Ca e.g. 5-100 ppm Ca but especially at least 100 ppm Ca such as 100-400 ppm e.g. 150-300 ppm Ca with at least 2 ppm Mg e.g. 2-20 ppm Mg but especially at least 20 ppm Mg such as 20-50 ppm Mg. In addition the bleach medium also usually contains aluminium and/or transition metal ions e.g. iron and/or manganese usually in amounts of at least 3 ppm of Fe and/or Mn and/or Al and at least 5 ppm in total e.g. 5-15 ppm each but especially at least 15 ppm in total e.g. 15-50 ppm (based on the total weight of pulp including water).

The bleach operation is usually performed at a temperature of 20-150°C especially 50-80°C at an initial pH of 10-11.5, which reduces to 6-10 by the end of the operation which usually takes 0.5-4 hr.

The compositions as hereinbefore described may also be used in a method of bleaching fabrics woven, spun or knitted from cellulosic fibres such as natural fibres e.g. cotton, ramie or flax, regenerated fibres e.g. viscose or cuprammonium rayon fibres, or blended fibres wherein one fibre is mixed with an amount e.g. a minority amount (such as 1-50%) of a coblendable fibre such as other material fibres such as wool or synthentic fibres such as polyester, polyamide or acrylic such as modacrylic fibres. Thus blends of 60-80% cotton with 20-40% polyester may be used. Suitable fabrics for bleaching may have a weight of 0.05-1.00 Kg/m² such as 0.1-1.00 Kg/m² but usually 0.15-0.40 Kg/m². The substrate fibres may also be in the form of thread or non woven fibres. In a fabric the warp and weft fibres are preferably the same, but may be different. The fabrics bleached by this method may for example be cotton or cotton polyester shirting or sheeting or curtain fabric. In the bleaching method the fabric may be treated for from 0.1 second to 2 minutes in a peroxide bath maintained at 50-150°C e.g. 70-110°C most usually 85-90°C containing from 0.5-4% e.g. 1-2% of hydrogen peroxide and from 10-200% e.g. 25-75% (based on the amount of the amount of peroxide) of a composition of components (b) and (c) as hereinbefore described and preferably

also a wetting agent especially a volatile wetting agent . Alternatively the bath composition as hereinbefore described may be sprayed straight onto the fabric. The process may be continuous or batchwise, may be repeated onc or more and may optionally be followed by heating and/or neutralisation with e.g. citric acid and/or rinsing and/or drying steps. The bleaching process may continue after the material has been removed from the bath, and even until the material is rinsed.

The method of the invention can provide a bleached cellulosic material e.g. pulp or fabric of desired brightness with minimum number and amount of additives, particularly the synergistic mixture of phosphonic acid (or salt) and phosphoric acid (or salt), especially in relation to commercial silicate processes.

The invention is illustrated in the following Examples, in which in Examples 1-6 the amounts of additives (dosages) are expressed in terms of the dry weights of the additives against the dry weight of the pulp.

Example 1

Stabiliser compositions were prepared by mixing an aqueous solution of partly neutralised DTPMPA (as its disodium salt), and orthophosphoric acid with water, in various proportions.

A thermomechanical wood pulp produced with hard water had a consistency of 24% (76% water) and contained 4 Fe, 47 Mn, less than 6 in total of Cu, Ni, Co, 260 Ca and 47 Mg, the amounts being expressed as ppm on the pulp (ie not on dry pulp). The pulp was diluted with bleach liquor to give a bleach medium of 15% consistency and containing 2.5 Fe, 29 Mn, less than 4 in total of Cu, Ni, Co, 163 Ca and 29 Mg ppm on the total medium. The bleach liquor contained 0.8% (expressed on dry pulp) of the stabiliser mixtures having a variety of proportions of DTPMPA and phosphoric acid and the rest water in amounts shown below, and 2% hydrogen peroxide (expressed by weight as hydrogen peroxide on the weight of dry pulp), as well as amounts of sodium hydroxide so that the initial pH of the bleach medium was in the range 10-10.8. The bleaching operation was performed at 60 °C for 2 hours. After the the bleach operation, the bleached pulp was converted into sheets, whose brightness level was determined according to TAPPE and the results expressed in ISO units. The brightness of the paper made from the unbleached pulp was also tested and found to be 53.9 ° ISO. The table below shows the results obtained. The contents of the DTPMPA (as dry solid) andphosphoric acid (as anhydrous material) in the bleach medium are expressed in terms of the dry weight of the pulp.

EXPERIMENT	In Stabiliser		In Bleached Medium			Brightness °ISO
	WT% of DTPMPA	Wt% of Phosphoric	Wt% DTPMPA	Wt% Phosphoric	Wt% Total	
A	13.5	50	0.11	0.40	0.51	66.6
B	13.5	33	0.11	0.27	0.37	65.9
C	9	50	0.07	0.40	0.47	66.3
D	9	33	0.07	0.27	0.34	65.3
E	9	27	0.07	0.22	0.29	64.9
F	4.5	49	0.04	0.40	0.43	65.9
G	4.5	33	0.04	0.27	0.30	64.8
Comp H	45	0	0.36	0	0.36	64.1
Comp J	28.1	0	0.22	0	0.22	63.8
Comp K	0	66	0	0.53	0.53	65.1

The initial pH values in the bleach media were 10.5, 10.3, 10.5, 10.4, 10.4, 10.3, 10.2, 10.8, 10.2 and 10.0 for Experiment A-K respectively, the pH values varying between the experiments in order to obtain an overall peroxide consumption in each case in the 2 hours of 70 ± 5%

Example 2

The process of Example 1 was repeated with a different pulp, different bleach conditions and different

amounts of stabiliser.

The pulp was a chemithermomechanical pulp produced with hard water and of 20.4% consistency (79.6% water)containing in ppm based on the wet pulp 16 Fe, 9 Mn, less than 6 in total of Co, Cu, Ni, 280 Ca and 45 Mg. The pulp was diluted with bleach liquor to 15% consistency to give the bleach medium containing 12 Fe, 7 Mn, less than 4 in total of Cu, Co, Ni, 206 Ca amd 33 Mg (expressed in ppm on the total bleach medium).

The bleach liquor contained the stabiliser mixtures in varying proportions and 4% hydrogen peroxide (based on dry pulp) and sodium hydroxide so that the pH of the bleach medium obtained was about 11. The bleaching operation was performed at 60° C for 4 hours. The brightness of unbleached pulp was 56.2° ISO.

The results, expressed as before, were as follows:

EXPERIMENT	In Stabiliser		In Bleached Medium			Brightness
	WT% of DTPMPA	Wt% of Phosphoric	Wt% DTPMPA	Wt% Phosphoric	Wt% Total	
L	9	27	0.18	0.54	0.72	79.4
M	13.5	33	0.20	0.50	0.70	79.5
N	9	27	0.22	0.68	0.90	80.2
Comp P	(sodium silicate (53° Baume) solution at 4% on pulp				1.88	79.5
Comp Q	0	66	0	1.33	1.33	73.9
Comp R	45	0	0.23	0	0.23	76.4

The initial pH values in the bleach media for Experiments K-P were 11.2, 10.9, 11.0, 11.0, 10.5 and 10.9 respectively, the pH values varying between the experiments in order to obtain an overall peroxide consumption in each case in the 4 hours of 75 ± 5%.

Example 3(a)

A peroxide stabilising composition was prepared by mixing the following ingredients, and its pH was then measured as 5.4.

Diethylene triamino pentamethylene phosphonic acid	9.0%
Phosphoric acid	27.2%
Sodium hydroxide	15.0%
Water	To 100%

Example 3(b)

In a continuous paper pulp bleaching process plant in which the chemithermomechanically produced paper pulp had metal ion concentrations of Fe 13ppm, Mn 7ppm, Co<2ppm, Cu<2ppm, Ni<2ppm, Ca 244ppm, Mg 29ppm, Na 868ppm, K 75ppm, Al 324ppm (based upon the wet weight of the bleach medium), the sodium silicate normally used as the peroxide stabiliser was replaced by the composition of Example 3(a). The paper pulp bleaching medium was sampled before and after the replacement of the sodium silicate. The brightness of each sample was monitored with time without further addition of additives. The conditions of bleaching and the brightness were as shown below. This pulp had an average unbleached brightness of 60.3° ISO.

Comparitive results

Additive	Continuous dosage rate	Time elapsed since sample removed/min	pH	Brightness /°ISO
Sodium hydroxide	2.18%			
Hydrogen peroxide	2.27%	60	9.1	70.0
Sodium silicate	3.2%	120	9.0	71.1
		180	8.8	72.5
Consistency	21.48%			
Temperature	56°C			

Sample taken 7.5 hours after initial addition of composition of Example 3(a)

Additive	Continuous dosage rate	Time elapsed since sample removed/min	pH	Brightness /°ISO
Composition (example 3(a)	2.2%			
Hydrogen peroxide	2.28%	60	9.2	74.4
Sodium hydroxide	2.59%	120	9.1	74.9
		180	8.6	76.2
Consistency	21.40%			
Temperature	60°C			

Example 4

In an experiment substantially the same as that described in Example 3(b) but with different dosage rates of peroxide and peroxide stabiliser, the following results were obtained. This pulp had an average unbleached brightness of 66.2 ° ISO

Comparative results

Additive	Continuous dosage rate	Time elapsed since sample removed/min	pH	Brightness /°ISO
Sodium Silicate	4.0%			
Sodium Hydroxide	3.2%			
Hydrogen peroxide	4.9%			
		60	9.6	79.0
Consistency	13.57%	120	9.4	80.6
		180	9.1	80.9
Temperature	57° C	240	9.0	81.2

Sample taken after 4 hours 15 minutes

Additive	Continuous dosage rate	Time elapsed since sample removed/min	pH	Brightness /°ISO
Hydrogen peroxide	4.7%			
Sodium hydroxide	3.5%			
Composition		60	9.7	77.7
(example 3(a)	2.0%	120	9.6	80.2
		180	9.45	81.3
Consistency	13.10%	240	9.15	81.8
Temperature	56°C			

Example 5

The process of Example 1 was repeated at 60° C upon a portion of thermomechanically produced paper pulp manufactured using hard water. The following results wre recorded. The pulp had a consistency of 15% and an analysis as follows

Metal	Fe	Mn	Co	Cu	Ni	Al	Ca	Mg	Na	K
metal concentration in bleach medium/ppm	3	29	<2	<2	<2	3	163	29	20	60

Additive	Dosag	
Hydrogen peroxide	2.0%	
Sodium hydroxide	1.6%	
Phosphoric acid	0.41%	
Diethylene triamino pentamethylene phosphonic acid	0.11%	
	Sample age 0 min	Sample age 120 min
pH	10.5	7.2
Brightness/° ISO	53.9	66.6

Example 6

The process of Example 1 was repeated at 60° C upon a portion of thermomechanically produced paper pulp manufactured using hard water. The following results were recorded. The pulp had a consistency of 15% and an analysis as follows with metal ion concentrations as recorded for Exmaple 3(b).

Additive	Dosage
Hydrogen peroxide	2.0%
Sodium hydroxide	1.6%
Phosphoric acid	0.41%
Diethylene triamino pentamethylene phosphonic acid	0.11%

	Sample age 0 min	Sample age 240 min
pH	10.9	9.0
Brightness/° ISO	62.0	80.0

Claims

1. A stabilised peroxide composition which comprises component (a) hydrogen peroxide, component (b) which is a water soluble amino organic phosphonic acid with at least 2 organo phosphonic acid groups, or a water soluble salt thereof, and component (c) which is orthophosphoric acid or a water soluble salt thereof.

2. A composition according to claim 1 wherein component (b) is a compound of formula (I) or a partially

or wholly neutralised salt thereof

$H_2O_3PCR^1R^2N(R^3)[R^4N(R^7)]_nCR^5R^6PO_3H_2$ (I)

wherein each of R^1, R^2, R^5, R^6, which are the same or different, represents a hydrogen atom or an optionally substituted aliphatic hydrocarbyl, alicyclic, aryl or aralkyl group, and each of R^3 and R^7, which is the same or different, is as defined for any one of R^1, R^2, R^5 and R^6 apart from hydrogen, or is a group of formula

$-C(R^8)(R^9)PO_3H_2$

wherein each of R^8 R^9, which may be the same or different, is as defined for any of R^1, R^2, R^5 or R^6, and R^4 represents a divalent organic group, n is 0 or an integer of at least 1, the weight ratio of component (c) (expressed as anhydrous acid) to component (b) (expressed as phosphonic acid) being 1.5-20:1.

3. A composition according to claim 1 or 2 wherein the weight ratio of component (c) (expressed as anhydrous acid) to component (b) (expressed as phosphonic acid) being 2-20:1.

4. A composition according to any one of claims 1-3 wherein the molar ratio of compound (b) to compound (c) is from 1:8.77 to 1:117.

5. A composition according to any one of claims 1-4 wherein each of R^1, R^2, R^5 and R^6 is hydrogen, R^4 is an alkylene group and R^7 is a group of the formula $-CH_2PO_3H_2$.

6. A composition according to claim 5 wherein component (b) is diethylene triamine pentakis (methylene phosphonic acid) or a water soluble salt thereof.

7. A composition according to any one of claims 1-6 wherein the weight ratio of components (b):(c) is from 1:2 to 1:10.

8. A composition according to any one of claims 1-6 wherein the weight ratio of components (b):(c) is from 1:6.75 to 1:10.

9. A composition according to any one of claims 1-8 which is substantially free of monomeric polyhydroxycarboxylic acids.

10. A composition according to any one of claims 1-9 wherein the weight proportion of components (a):-(b):(c) is 100: (1 to 10): (5 to 35).

11. A composition according to any of claims 1-10 consisting essentially of compounds (a), (b), (c) and water.

12. A pulp bleaching medium which comprises an aqueous medium containing a cellulosic pulp and a composition according to any of claims 1-11.

13. A method of bleaching a cellulosic material with hydrogen peroxide, wherein the cellulosic material is contacted with an aqueous alkaline solution comprising as component (a) the hydrogen peroxide, component (b) which is a water soluble amino phosphonic acid, or water soluble salt of an amino phosphonic acid, and component (c) which is orthophosphoric acid or a water soluble orthosphosphate salt.

14. A method according to claim 13 wherein the cellulosic material is contacted with an aqueous solution of a composition as claimed in any one of claims 2-11.

15. A method according to claim 13 or 14 wherein the mixture of aqueous alkaline solution and cellulosic material which forms a bleach medium contains at least 15 ppm in total of transition metals and aluminium.

16. A method according to any one of claims 13-16 wherein the mixture of the aqueous alkaline solution and cellulosic material which forms a bleach medium contains at least 100 ppm of calcium and at least 20 ppm of magnesium.

17. A method according to any one of claim 13-16 wherein the cellulosic material is mechanically or thermo mechanically prepared wood pulp.

18. A method according to claim 17 wherein the pulp is treated at 50-80° C for 0.5-4 hr.

19. A method according to claim 17 or 18 wherein the aqueous solution contains 0.5-10% component (a), 0.005-1% component (b) and 0.025-3.5% of component (c).

20. A method according to any one of claims 17-19 wherein the amount of component (c) is greater than 0.22% when expressed as anhydrous phosphoric acid with respect to dry weight of cellulosic material.

21. A method according to any one of claims 13-16 wherein the cellulosic material is a cellulosic woven textile fabric.

22. A method according to claim 21 wherein the fabric is contacted at 80-150° C for from 0.1 seconds to 2 mins.

23. A method according to claims 21 or 22 wherein the cellulosic woven textile fabric is contacted with a bleaching composition additionally containing a wetting agent.

24. Use of a mixture of components (b) and (c) as defined in any one of claims 1-11 as a stabiliser for hydrogen peroxide in the bleaching of cellulosic material.

25. A pulp bleaching medium which comprises a cellulosic pulp and an aqueous alkaline medium as

defined in claim 1.

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(54) Phosphate composition and uses thereof.

(57) The brightness of hydrogen peroxide bleached cellulosic material e.g. mechanical wood pulp or fabrics may be increased if the cellulosic material is contacted with both phosphoric acid, or a salt thereof, and an amino phosphonic acid or a salt thereof.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 141 355 (BENCKISER-KNAPSACK GmbH) * Whole document *	1-8,11-14,18,19,24,25	D 21 C 9/16 D 21 C 9/10 D 06 L 3/02
X	DE-A-3 531 563 (BENCKISER-KNAPSACK GmbH) * Whole document *	1-8,11-15,17-19,24,25	
A	US-A-4 294 575 (MONSANTO CO.) * Whole document *	1-8,11-17,18,21,22,24,25	
A	EP-A-0 186 990 (DOW CHEMICAL) * Page 1 - page 7, line 14; claims 1-6,12-14 *	1-6,11-14,21,24,25	
A	TAPPI JOURNAL OF THE TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY, vol. 71, no. 6, June 1988, pages 171-174, Nocross, Ga, US; K. KUCZYNSKI et al.: "DTPMPA: polyamino polyphosphonic acid and its use in paper processes. Part 1: The chemistry of pulp bleaching with DTPMPA and its impact on fines retention" * Whole document *	1,2,5,6,9-14,17-19,24,25	TECHNICAL FIELDS SEARCHED (Int. Cl.5) D 21 C D 21 H D 06 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-09-1990	BERNARDO NORIEGA F.

CATEGORY OF CITED DOCUMENTS

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